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**(54) Multi-step process to incorporate grain growth inhibitors in WC-Co composite**

(57) Grain growth inhibitors including vanadium carbide, chromium carbide, tantalum carbide, and niobium carbide are incorporated into a cobalt/tungsten carbide matrix during the formation of the cobalt/tungsten carbide matrix. A precursor powder is formed by combining in solution a cobalt composition, a tungsten composition and a grain growth inhibiting metal composition, which is then spray dried. The precursor compound is then car-

burized in carbon monoxide and carbon dioxide to form cobalt/tungsten carbide matrix. This is then further carburized in a hydrocarbon hydrogen gas at an elevated temperature to cause the grain growth inhibiting metal present to form the carbide. The second carburizing step is conducted with a carburizing gas having a carbon activity greater than about 2 for a relatively short period of time at 900° C to 1000° C.

EP 0 834 589 A1

## Description

Cemented carbide articles such as cutting tools, mining tools, and wear parts are routinely manufactured from carbide powders and metal powders by the powder metallurgy techniques of liquid phase sintering or hot pressing. Cemented carbides are made by "cementing" hard tungsten carbide (WC) grains in a softer fully-dense metal matrix such as cobalt (Co) or nickel (Ni).

The requisite composite powder can be made in two ways. Traditionally, WC powder is physically mixed with Co powder in a ball mill to form composite powder in which WC particles are coated with Co metal. A newer way is to use spray conversion processing, in which composite powder particles are produced directly by chemical means. In this case, a precursor salt in which W and Co have been mixed at the atomic level, is reduced and carbonized to form the composite powder. This method produces powder particles in which many WC grains are imbedded in a cobalt matrix. Each individual powder particle with a diameter of 50 micrometers contains WC grains a thousand times smaller.

The next step in making a cemented carbide article is to form a green part. This is accomplished by pressing or extruding WC-Co powder. The pressed or extruded part is soft and full of porosity. Sometimes further shaping is needed, which can be conveniently done at this stage by machining. Once the desired shape is achieved, the green part is liquid phase sintered to produce a fully dense part. Alternatively, a fully-dense part is sometimes produced directly by hot pressing the powder. In a final manufacturing step, the part is finished to required tolerances by diamond grinding.

Cemented carbides enjoy wide applicability because the process described above allows one to control the hardness and strength of a tool or part. High hardness is needed to achieve high wear resistance. High strength is needed if the part is to be subjected to high stresses without breaking. Generally, cemented carbide grades with low binder levels possess high hardness, but have lower strength than higher binder grades. High binder levels produce stronger parts with lower hardness. Hardness and strength are also related to carbide grain size, the contiguity of the carbide grains and the binder distribution. At a given binder level, smaller grained carbide has a higher hardness. Trade-off tactics are often adopted to tailor properties to a particular application. Thus, the performance of a tool or part may be optimized by controlling amount, size and distribution of both binder and WC.

The average WC grain size in a sintered article will not, generally, be smaller than the average WC grain size in the powder from which the article was made. Usually, however, it is larger because of grain growth that takes place, primarily, during liquid phase sintering of the powder compact or extrudate. For example, one can start with 50 nanometer WC grains in a green part and end up with WC grains larger than 1 micrometer.

A major technical challenge in the art of sintering is to limit such grain growth so that finer microstructures can be attained. Thus, it is typical to add a grain growth inhibitor to WC-Co powder before it is compacted or extruded. The two most commonly used grain growth inhibitors are vanadium carbide (VC) and chromium carbide ( $\text{Cr}_3\text{C}_2$ ) with TaC and NbC used less frequently. However, the use of these additives presents some problems. First, both are particularly oxygen sensitive, and when combined with WC and binder metal in a mill, both tend to take up oxygen, forming surface oxides. Later, during the liquid phase sintering step, these oxides react with carbon in the mixture to form carbon monoxide (CO) gas. If extra carbon has not been added to the powder to allow for this consumption of carbon, then this results in the WC and Co forming brittle  $\eta$ -phases, which ruins the article. If too much carbon has been added, so-called carbon porosity results, again ruining the article. Even if just the right amount of carbon has been added, the evolution of CO gas itself can lead to unacceptable levels of porosity. High oxygen levels in powder compacts or extrudates lead to major problems during their sintering.

The present invention is premised on the realization that grain growth inhibitors, including vanadium carbide, chromium carbide, niobium carbide and tantalum carbide can be incorporated into a cobalt/tungsten cobalt carbide matrix during the formation of the cobalt/tungsten cobalt carbide matrix. Suitable salts of vanadium, chromium, tantalum, niobium or mixtures thereof can be combined with cobalt and tungsten compounds, dissolved into solution, and spray dried to form precursor compounds. It has been found that the precursor compounds can be carburized using a two-step process to form tungsten carbide embedded in cobalt matrix, along with the carbides of vanadium, chromium, tantalum and/or niobium, while retaining the fine grain structure in the powder.

The carburization process requires a two-step process. In a preferred embodiment, in the initial process a relatively low carbon activity gas formed from carbon monoxide and carbon dioxide is used at relatively low temperatures -- about 750°C to 850°C. This is continued until the tungsten is completely reacted to form tungsten carbide. This will leave the grain growth inhibitor composition as an oxide. The carburization is then continued using a gas having a higher carbon activity, specifically a combination of hydrogen and a hydrocarbon at a higher temperature, about 850°C to 950°C, for no more than one hour. This will quickly cause the grain growth inhibiting composition to change from an oxide to a carbide without adversely affecting the previously-formed tungsten carbide/cobalt matrix. This allows the grain growth inhibitor to be directly formed with the cobalt/tungsten carbide matrix providing for more uniform distribution, less oxide formation, less oxygen sensitivity, and retention of fine grain size. This also reduces processing steps. The objects and advantages of the present inven-

tion will be further appreciated in light of the following detailed description.

According to the present invention, a tungsten carbide/cobalt matrix is formed which has evenly distributed throughout a grain growth inhibiting composition which is a carbide of vanadium, chromium, niobium, tantalum and mixtures thereof. In order to form these compounds, a precursor particle is formed. The precursor particle is simply a spray-dried particle which is formed from a solution having dissolved therein a cobalt composition, a tungsten composition and a composition of one or more of vanadium, chromium, tantalum and niobium.

The process of forming the precursor particles is disclosed in *McCandlish et al.* U.S. Patent 5,352,269. The purpose is to form a solution that contains cobalt, tungsten, as well as the grain growth inhibiting metal. This solution can be formed with any solvent, but for environmental reasons it is preferred that the solvent be water. Therefore, preferably all the compositions will be water-soluble. If, for some reason, it is desired to use a different solvent such as a hydrocarbon solvent, then water-insoluble, hydrocarbon-soluble compositions would be employed.

With respect to cobalt, the cobalt is preferably added using a precursor composition such as cobaltous chloride, cobaltous nitrate, or cobaltous acetate. Tungsten compositions that are suitable for use in the present invention would be ammonium metatungstate, triethylenediamine cobalt tungstate (which provides both cobalt and tungsten), as well as tungstic acid, preferably dissolved in ammonium hydroxide.

The grain growth inhibiting compositions suitable for use in the present invention would be compositions of the metal such as acetates, carbonates, formates, citrates, hydroxides, nitrates, oxides, formates and oxalates. These are all combined in the desired proportions to form the cobalt/tungsten carbide matrix with the desired amount of grain growth inhibiting carbide. Generally, from about 0.15% to about 5% (preferably less than 3%) of the grain growth inhibiting carbide will be present in the formed composition. Generally, there will be about 2% to about 20% cobalt, with about 80% to about 97% tungsten by weight. Thus, the precursor solution is formed with these desired end ratios in mind.

The solution is then spray-dried to form homogeneous, discrete powder particles. Any type of spray drying apparatus can be employed. The goal is simply to provide small, uniform particles containing the cobalt, tungsten and grain growth inhibiting metal. This powder is then carburized in a gas mixture of carbon monoxide and carbon dioxide or hydrogen/carbon monoxide, according to the method disclosed in *McCandlish* U.S. Patent 5,230,729. The precursor particles are introduced into a reactor and heated in the presence of a carburizing gas. Many different reactors can be used. It is best to use a reactor that provides good contact of the carburizing gas with the particles. A fluidized bed reactor

as well as a rotary bed reactor can be used. Further, a fixed bed reactor can even be used, but this increases reaction time due to the decreased physical mixture of the carburizing gas.

Initially, the tungsten carbide is carburized. In this initial carburization, the carburizing gas is a combination of carbon monoxide and carbon dioxide or hydrogen/carbon monoxide, and the reaction temperature should be from about 750° C up to about 850° C, with 775-835° C preferred. Initially the carbon activity of the gas is established at > 1, preferably from about 1 to about 1.4, with about 1.2 being preferred. The carbon activity of the gas is adjusted by altering the ratio of carbon monoxide to carbon dioxide or carbon monoxide levels in hydrogen/carbon monoxide. This is continued for a period of about 2 hours, and then the carbon activity is reduced to below 1, preferably less than 0.5, preferably around 0.3. When the carbon activity is greater than 1, free carbon is deposited. Establishing the carbon activity at less than 1 will then drive off this free carbon. The reduced carbon activity reaction is continued for up to about 25 hours, and then the higher carbon activity reaction is resumed. This is cycled back and forth 4 to 7 times until the reaction is complete.

After the formation of the tungsten carbide is complete, the reaction conditions are modified to cause the grain growth inhibiting metal to form a carbide. In order to form the grain growth inhibiting carbide, the carburizing gas is changed and the temperature is changed. The second carburization gas must have a high carbon activity greater than 1.3, and preferably at least about 3.0. Further, the carburizing gas cannot contain oxygen. Accordingly, the carburizing gas is formed preferably from a hydrocarbon, in combination with hydrogen as a diluent. The hydrocarbon can be, for example, methane, ethane, propane, natural gas, ethylene, propylene, acetylene and the like, as long as it contains only hydrogen and carbon and no oxygen. The reaction temperature needs to be somewhat higher, preferably from about 900° C to 1000° C. This is continued for a relatively short period of time, preferably as brief as possible. The time will preferably be about less than 1 hour, depending upon the amount of grain growth inhibiting metal present. Typically, there will be from about 0.15% up to no more than 5% of the grain growth inhibiting metal. Therefore the conversion time is very rapid. After the second conversion step is complete, the product is then allowed to cool and can be subsequently processed into tungsten carbide tools and the like.

The present invention will be further appreciated in light of the following detailed examples.

#### EXAMPLE 1

Ten pounds of spray dried W-Co-Cr-V salts (WC 10% Co - 0.3% VC - 0.31% Cr<sub>3</sub>C<sub>2</sub>) are loaded into the tube furnace. Under nitrogen, the powder is heated to 850° C and carburized with hydrogen/30% carbon mon-

oxide. Excess free carbon is removed by adding 12% carbon dioxide to the gases (4 minutes for each hour). After 16 hours, the temperature is raised to 900° C and a gas mixture of hydrogen (10%) methane is applied for 1 hour. Cooling is then done under nitrogen. This results in the formation of WC-Co-VC-Cr<sub>3</sub>C<sub>2</sub>. The grain growth inhibitors are evenly distributed throughout the matrix.

Thus the present invention provides a method of incorporating grain growth inhibitors into a tungsten carbide/cobalt matrix, which in turn permits these products to be further sintered and processed while grain growth is minimized. The processing steps of the present invention allow the grain growth inhibitor to be uniformly dispersed throughout the product and further minimizes the oxygen sensitivity or overall effect of oxygen on the formed product.

#### Claims

1. A method of forming cobalt/tungsten carbide particles containing a carbide of a grain growth inhibiting metal selected from the group consisting of vanadium, chromium, tantalum and niobium from a precursor powder containing cobalt, tungsten and at least one of the grain growth inhibiting metals, the method comprising subjecting the precursor powder to an initial carburization with a carburizing gas comprising a mixture of carbon monoxide and carbon dioxide at a temperature effective to form tungsten carbide, and a second carburization step using a carburizing gas comprising a diluent and a hydrocarbon gas having a carbon activity greater than about 1.4 at a temperature of about 900°C to 1000°C.
2. A method as claimed in Claim 1 wherein the initial carburization is conducted at a temperature of from about 750°C to about 850°C.
3. A method as claimed in either Claim 1 or Claim 2 wherein the second carburization is conducted for a period of about 1 to about 3 hours.
4. A method as claimed in any preceding Claim wherein the initial carburization is conducted with a first gas having a carbon activity of greater than 1 for a first period of time, and subsequently with a second gas having a carbon activity less than 1 for a second period of time.
5. A method as claimed in any preceding Claim wherein the precursor powders are formed by combining in solution a cobalt compound, a tungsten compound, and a precursor metal compound and spray drying the solution to form the precursor compound.
6. The product made by the process claimed in any preceding Claim.
7. A cobalt/tungsten carbide matrix comprising a cobalt matrix having embedded therein uniformly dispersed particles of tungsten carbide on a surface of the cobalt, and further having uniformly dispersed grain growth inhibiting metal carbide particles throughout the surface of said cobalt, wherein said grain growth inhibiting metal is selected from the group consisting of vanadium, chromium niobium and tantalum.
8. A matrix as claimed in Claim 7 comprising from about 0.15% to about 5% grain growth inhibiting metal carbide.
9. A matrix as claimed in Claim 8 having from about 0.15% to 3% VC.
10. A matrix as claimed in Claim 8 having from about 0.15% to 3% Cr<sub>3</sub>C<sub>2</sub>.
11. A matrix as claimed in any one of Claims 7 to 10 comprising from about 2% to about 20% cobalt.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 97 30 7254

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	WO 96 24454 A (SANDVIK AB) * example 3 *	7,11	C22C29/08
A	* page 3, line 24 - page 4, line 21 *	1,8-10	
X	DE 44 14 135 A (KOBELSTEEL LTD) * claims 1-4 *	7-11	
A	* examples 1,5-8 *	1	
A	WO 91 07244 A (PROCEDYNE CORP ; UNIV RUTGERS (US)) * claims 1-14 *	1	
D	* page 26, line 5 - line 18 * & US 5 352 269 A (MC CANDLISH ET AL.)		
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C22C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 December 1997	Examiner Rigondaud, B
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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